

# **Bench-scale Kinetics Study of Mercury Reactions in FGD Liquors**

## **Semiannual Technical Progress Report**

**April 1, 2005 – September 30, 2005**

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## ABSTRACT

This document summarizes progress on Cooperative Agreement DE-FC26-04NT42314, “Kinetics Study of Mercury Reactions in FGD Liquors,” during the time-period April 1, 2005 through September 30, 2005. The project is being co-funded by the U.S. DOE National Energy Technology Laboratory and EPRI. URS Group is the prime contractor.

The objective of the project is to determine the mechanisms and kinetics of the aqueous reactions of mercury absorbed by wet flue gas desulfurization (FGD) systems, and develop a kinetics model to predict mercury reactions in wet FGD systems. The model will be used to determine optimum wet FGD design and operating conditions to maximize mercury capture in wet FGD systems and to ensure that mercury leaves the system in the byproduct solids rather than in blow down liquor.

A series of bench-top, liquid-phase reactor tests are being conducted and mercury species concentrations measured by UV/visible light spectroscopy to determine reactant and byproduct concentrations over time. Other measurement methods, such as atomic absorption, are being used to measure concentrations of species that cannot be measured by UV/visible light spectroscopy.

These data will be used to develop an empirically adjusted, theoretically based kinetics model to predict mercury species reactions in wet FGD systems. The model will be verified in tests conducted with a bench-scale wet FGD system, where both gas-phase and liquid-phase mercury concentrations will be measured to determine if the model accurately predicts the tendency for mercury re-emissions and the phase in which mercury is found in the FGD byproducts. The model will be run over a wide range of potential wet FGD design and operating conditions to determine conditions that maximize mercury capture, minimize mercury re-emissions, and/or ensure that mercury captured leaves the system in the byproduct solids rather than in blow down liquor.

This is the second reporting period for the subject Cooperative Agreement. During this period, two presentations of project results were made, one at the DOE/NETL Mercury Control Technology R&D Program Review meeting, at one at the Air Quality V symposium. Reaction kinetics measurements have been conducted using several measurement techniques, using a UV/visible light spectrometer to track liquid-phase species concentrations and atomic absorption to measure elemental mercury release rates. Work during this period has focused on the effects of chloride, thiosulfate ion, and of ionic strength on re-emissions reaction mechanisms and kinetics. The formation of a chloro-mercuric sulfite complex has been identified. The data collected are continually used to update an initial form of the kinetics model. Reactions involving the chloro-mercuric sulfite complex have been added to the model. No bench-scale wet FGD tests have been conducted yet; these are planned for the next semi-annual period.

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## INTRODUCTION

This document summarizes progress on Cooperative Agreement DE-FC26-04NT42314, “Kinetics Study of Mercury Reactions in FGD Liquors,” during the time-period April 1, 2005 through September 30, 2005. The project is being co-funded by the U.S. DOE National Energy Technology Laboratory and EPRI. URS Group is the prime contractor.

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A series of bench-top, liquid-phase reactor tests are being conducted and mercury species concentrations measured by UV/visible light spectroscopy to determine reactant and byproduct concentrations over time. Other measurement methods, such as atomic absorption, are being used to measure concentrations of species that cannot be measured by UV/visible light spectroscopy, such as elemental mercury as it is released from the liquid phase due to re-emission reactions. These data are being used to develop an empirically adjusted, theoretically based kinetics model to predict mercury species reactions in wet FGD systems. The model will be verified in tests conducted with a bench-scale wet FGD system, where both gas-phase and liquid-phase mercury concentrations will be measured to determine if the model accurately predicts the tendency for mercury re-emissions and the phase in which mercury is found in the FGD byproducts.

The model will be run over a wide range of potential wet FGD design and operating conditions to determine conditions that maximize mercury capture, minimize mercury re-emissions, and/or ensure that mercury captured leaves the system in the byproduct solids rather than in blow down liquor.

This is the second reporting period for the subject Cooperative Agreement. During this period, two presentations of project results were made, one at the DOE/NETL Mercury Control Technology R&D Program Review meeting, at one at the Air Quality V symposium. Reaction kinetics measurements have been conducted using several measurement techniques, using a UV/visible light spectrometer to track liquid-phase species concentrations and atomic absorption to measure elemental mercury release rates. Work during this period has focused on the effects of chloride, thiosulfate ion, and of ionic strength on re-emissions reaction mechanisms and kinetics. The formation of a chloro-mercuric sulfite complex has been identified. The data collected are continually used to update an initial form of the kinetics model. Reactions involving the chloro-mercuric sulfite complex have been added to the model. No bench-scale wet FGD tests have been conducted yet; these are planned for the next semi-annual period. This report presents and discusses these project results.

The remainder of this report is divided into five sections: an Executive Summary followed by a section that describes Experimental procedures, then sections for Results and Discussion, Conclusions, and References.

## **EXECUTIVE SUMMARY**

### **Summary of Progress**

The current reporting period, April 1, 2005 through September 30, 2005, is the first technical progress reporting period for the project. During this period, two presentations of project results were made, one at the DOE/NETL Mercury Control Technology R&D Program Review meeting, at one at the Air Quality V symposium. Reaction kinetics measurements have been conducted using several measurement techniques, using a UV/visible light spectrometer to track liquid-phase species concentrations and atomic absorption to measure elemental mercury release rates. Work during this period has focused on the effects of chloride, thiosulfate ion, and of ionic strength on re-emissions reaction mechanisms and kinetics. The formation of a chloro-mercuric sulfite complex has been identified. The data collected are continually used to update an initial form of the kinetics model. Reactions involving the chloro-mercuric sulfite complex have been added to the model. No bench-scale wet FGD tests have been conducted yet; these are planned for the next semi-annual period.

### **Problems Encountered**

There were no significant problems encountered during the reporting period.

### **Plans for Next Reporting Period**

The next reporting period (October 1, 2005 through March 31, 2006), would be the final reporting period, as the project period of performance currently ends on March 31, 2006. However, it is likely that a no-cost-increase extension to the period of performance will be requested. During this next period, the Task 2 reaction kinetics tests will be completed, and these data will be used to complete an empirically adjusted, theoretically based kinetics model to predict mercury species reactions in wet FGD systems. Task 3 will be conducted, wherein the model will be verified in tests conducted with a bench-scale wet FGD system. Both gas-phase and liquid-phase mercury concentrations will be measured to determine if the model accurately predicts the tendency for mercury re-emissions and the phase in which mercury is found in the FGD byproducts. The model will be used to identify additives that could be used to reduce mercury re-emissions levels from wet FGD systems. These additives will also be investigated in the bench-scale wet FGD systems.

### **Prospects for Future Progress**

Assuming the period of performance is extended, the final reporting period will be used to complete the Task 3 bench-scale model verification tests. The only additional project efforts will be related to reporting, including preparation and submittal of the third semi-annual technical progress report and the project final report.



## EXPERIMENTAL

### Task 2: Kinetic Data Gathering and Initial Model Development

This project is collecting kinetic data under conditions specific to wet FGD systems. Kinetic measurements include liquors containing chloride and thiosulfate, both of which may form strong complexes with  $\text{Hg}^{+2}$ . Chloride is known to form a series of complexes with  $\text{Hg}^{+2}$ . Thiosulfate may complex and/or reduce  $\text{Hg}^{+2}$ . Effects of other major species in FGD liquors, such as sulfate and nitrate ions, will also be determined. Another important variable is pH, which affects both the distribution of sulfite species and the kinetics.

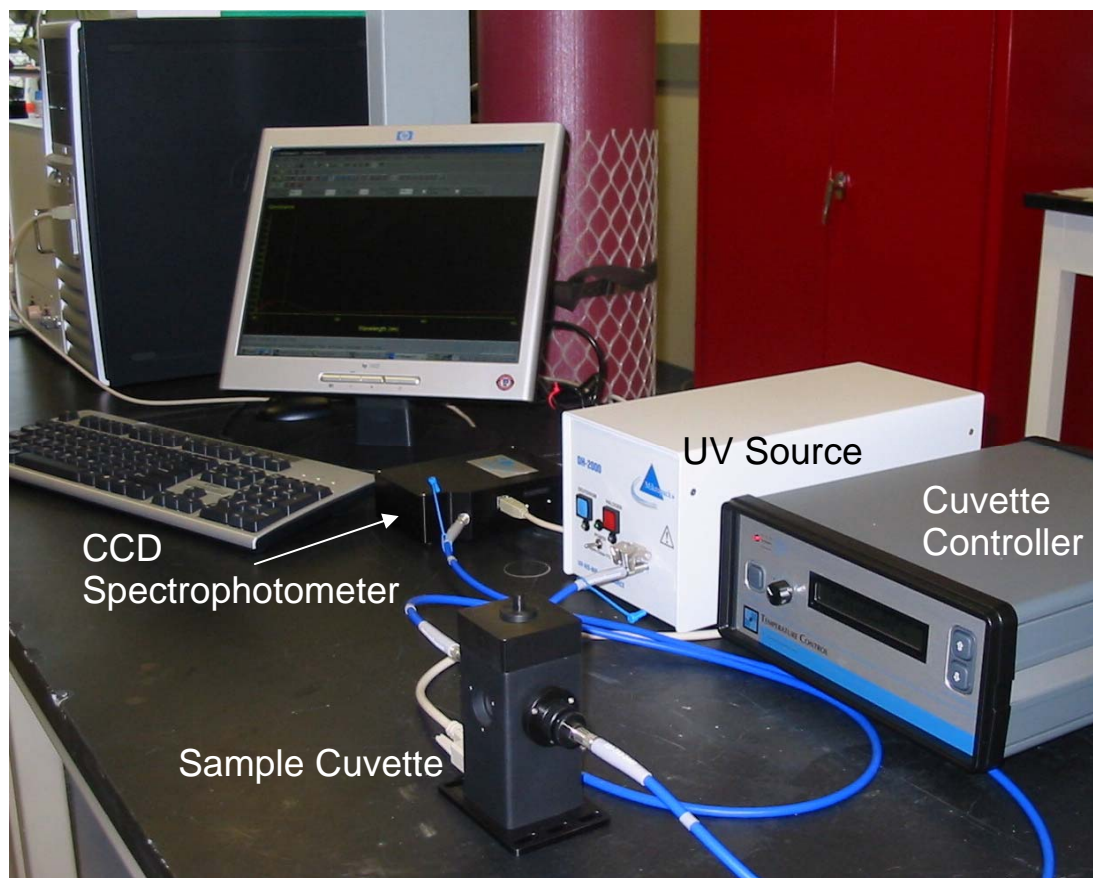
In addition to chemical species effects, the effects of temperature and ionic strength on kinetics are being determined. Temperature is always important for chemical kinetics. While the project is concentrating on the normal FGD temperature range (50-55°C), higher and lower temperatures will be investigated. This will improve the accuracy of activation energy values used in the model and ensure that the model results apply to FGD that operate at other temperatures (e.g., on lignite-fired plants that have a high flue gas saturation temperature).

Ionic strength is related to the total concentration of dissolved, ionic species in the liquor. Determining ionic strength effects is often helpful for determining reaction mechanisms and for modeling. The rate of reaction in a solution can be increased, decreased, or unchanged with increasing ionic strength, depending on whether the reactants in a rate-determining reaction step have the same or an opposite charge, or if one reactant is uncharged. Ionic strength dependence is normally determined by measuring rate constants as a function of added electrolyte concentration, using non-complexing electrolytes such as sodium perchlorate ( $\text{NaClO}_4$ ).

The key Hg-sulfite species have intense absorption peaks in the UV range and thus can be monitored as a function of time by taking periodic spectral measurements. Current instrumentation allows rapid gathering of complete UV/Vis spectra (nominally 50 spectra per second) or monitoring light absorbance at up to six wavelengths simultaneously, whichever is desired. This greatly enhances the ability to obtain both pathway information (by following multiple peaks in the spectra) and better kinetics data for construction of a meaningful model.

This has been done initially for model systems containing only a few species. As more information is obtained, it should be possible to extend these spectral methods to monitoring FGD solutions in the bench-scale FGD system, as described later in this section, and thus correlate the model results with liquid systems where good measurements of Hg absorption and re-emission are possible. This will prove especially valuable for evaluating additives intended to reduce re-emission of  $\text{Hg}^0$ .

The experimental apparatus for following aqueous reactants at low concentrations consists of a stirred spectrophotometric cell housed in a special cell holder which provides precise temperature control, stirring, inert gas flow as required, and fiber optic hookups to a UV/Vis light source and a CCD spectrometer. The spectrometer and cell holder are computer controlled, enabling precise control and rapid sampling. Figure 1 is a photograph of the bench-top spectrophotometric equipment.



**Figure 1. Photo of UV/Vis Spectrometer and Cell Holder Apparatus**

The spectrophotometric system used for kinetics measurements is built around an Ocean Optics HR2000 high-resolution miniature fiber optic spectrometer, which includes a Sony ILX511 linear CCD array detector. The spectrometer interfaces to the main computer. It is capable of providing full spectrum scans into memory every 13 milliseconds and has an integration time variable from 3 milliseconds to 65 seconds. The high resolution of the optical bench of this spectrometer is provided by an expanded 1-inch diameter, 4-inch focal length (f/4) design in a symmetrical crossed Czerny-Turner optical design.

The optical system uses an Ocean Optics DT-1000 deuterium tungsten halogen light source, which combines the continuous spectrum of a deuterium UV light source and a tungsten halogen Vis/shortwave near-infrared light source into a single optical path. The combined-spectrum light source produces a stable output from ~200-1100 nm. The output is coupled to a fiber optic for transmission to the cuvette (measurement cell) holder.

This kinetics work uses a Quantum Northwest TLC 50F™ fiber optic temperature-controlled cuvette holder in conjunction with the spectrometer and light source. The computer-controlled cuvette holder provides precise temperature control of the 1-cm cuvette reaction vessel, built-in magnetic stirring, a dry gas purge to limit condensation or exclude oxygen from the cuvette, and optical slits for control of the illuminated volume.

The package includes a Quantum Northwest TC 101 microprocessor-controlled temperature controller and is calibrated against a NIST-traceable thermometer. It uses a Peltier device for temperature control and is capable of maintaining the cuvette temperature at  $-40$  to  $+105^{\circ}\text{C}$   $\pm 0.02^{\circ}\text{C}$ .

Since the reactions studied thus far have been fairly slow, a simple but effective manual mixing method has been used to obtain kinetics data. Typically 2.00 mL of solution containing mercuric perchlorate and a pH buffer is placed in the spectrophotometric cell and temperature equilibrated in the cuvette holder. Continuous acquisition of spectra is initiated, typically taking a complete spectrum every five seconds. About 10 spectra are thus obtained for background subtraction purposes, and then a small amount of sulfite solution (typically 20-50  $\mu\text{L}$  using a microliter pipetter) is injected into the stirred spectrophotometric cell to start the reaction. This addition results in the abrupt appearance of a peak in the 230-235 nm region due to mercuric disulfite. The decay of this peak is then monitored by continuing to take spectra for up to several hours.

The spectrophotometric zero of absorbance is set before the run using pure water at the same temperature as the reaction and is checked after the timed run. When chloride is used it is added directly to the spectrophotometric cell before the sulfite, using microliter amounts of a concentrated sodium chloride (NaCl) solution. The pH buffers used are based on chloroacetic acid for pH 3.0 and acetic acid for higher pH, all at the 0.01 M level and adjusted to the desired pH using sodium hydroxide (NaOH) solution. The pH of the solution after the run is also checked using a pH probe inserted into the spectrophotometric cell. A relatively low buffer concentration is used to minimize secondary effects on the kinetics. Initial checks at pH 3 did not indicate any spurious buffer effects.

In unraveling complex chemical kinetics, it is important to measure as many of the participating chemical species as possible, including both reactants and products. Therefore, some tests also measure the production of  $\text{Hg}^0$  in solutions similar to those used for the UV/Vis spectrometer measurements, primarily by conducting gas phase Hg measurements. This will augment the results available for model fitting and will help determine if the Hg-SO<sub>2</sub> species actually exists and to further characterize it.

The test apparatus for following the formation of  $\text{Hg}^0$  consists of a reaction vessel (sparger) charged with an aqueous solution containing a buffer for pH control and other chemical species, such as chloride, as desired. A gas stream containing nitrogen, SO<sub>2</sub>, and presaturated with water is passed through this solution at a constant rate, typically 1.0 L/min. The SO<sub>2</sub> concentration in the gas and pH are chosen to give the desired SO<sub>2</sub> concentration in the liquid. The sparged reaction vessel is submerged in a water bath temperature controlled to  $\pm 0.1^{\circ}\text{C}$ . When steady state is reached, a solution containing mercuric ion is injected into the sparged solution via a hypodermic syringe and septum at "t = 0." This starts the reaction and elemental mercury sparged from the reaction vessel is measured using a UV gas cell spectrophotometer and a 254 nm mercury lamp (an atomic absorption analyzer). These measurements are done at regular time intervals using a computer controlled data acquisition system.

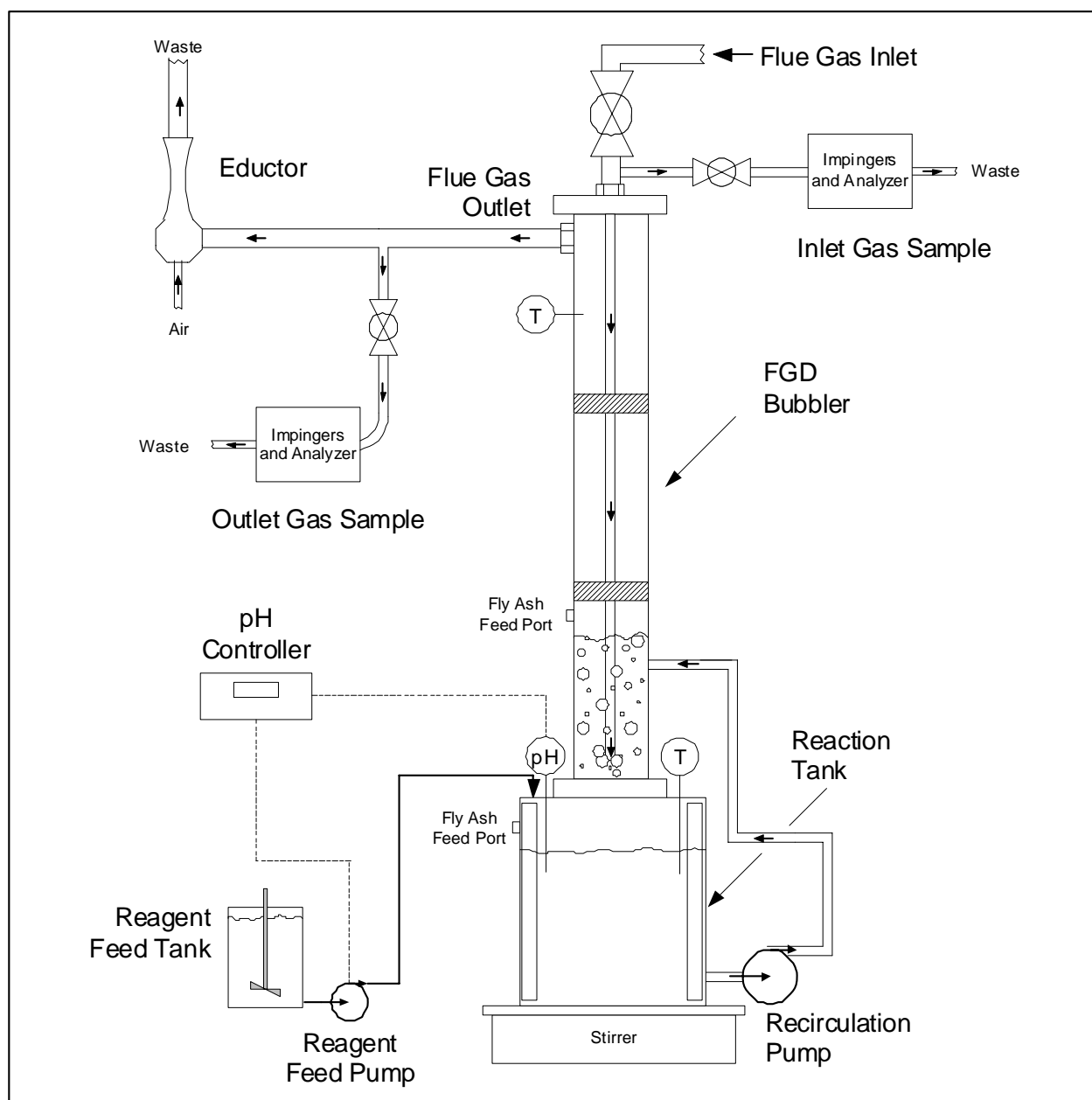
### **Task 3: Model Refinement, Bench-scale Validation and Additive Testing**

The kinetics data described above will be used to develop an empirically adjusted, theoretically based kinetics model to predict mercury species reactions in wet FGD systems. The model will be verified in tests conducted with a bench-scale wet FGD system, where both gas-phase and liquid-phase mercury concentrations will be measured to determine if the model accurately predicts the tendency for mercury re-emissions and the phase in which mercury is found in the FGD byproducts. The model will be used to identify additives that could be used to reduce mercury re-emissions levels from wet FGD systems. These additives will also be investigated in the bench-scale wet FGD systems.

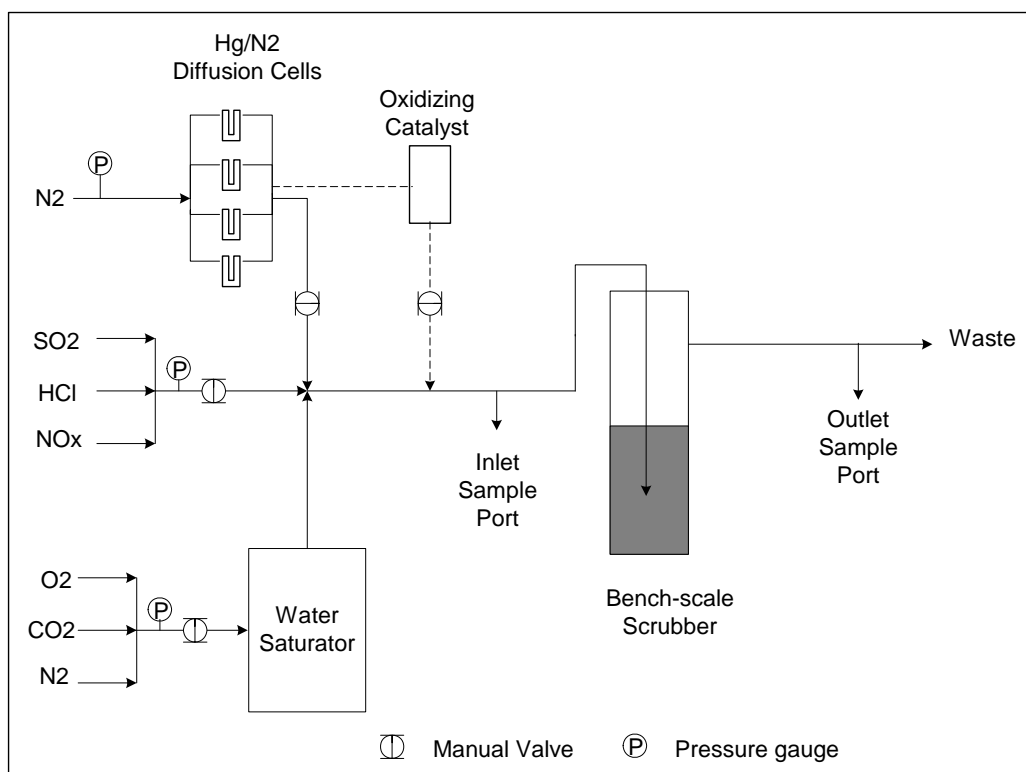
Prior to beginning this project, an existing bench-scale wet scrubber was modified to add a new absorber vessel with an integral reaction tank, a magnetic agitator drive for the reaction tank to allow the tank to be tightly sealed, and a venturi eductor to allow scrubber operation at negative gauge pressures. Figure 2 illustrates the revised 1-cfm (28-l/min) bench-scale scrubber to be used in the Task 3 bench-scale wet FGD simulation testing.

Simulated flue gas is mixed from a variety of compressed gases using calibrated rotameters. Figure 3 shows the simulation gas mixing apparatus. The dry simulation gas typically contains SO<sub>2</sub>, NO<sub>x</sub>, HCl, CO<sub>2</sub>, oxygen, and nitrogen. Moisture is added to the simulation gas by feeding the oxygen, CO<sub>2</sub>, and a portion of the dry nitrogen gas through a water saturator, which is maintained at a predetermined pressure and temperature to achieve the desired humidity level in the wet gas mixture.

Oxidized (or elemental) mercury is added to the gas by passing a portion of the dry nitrogen gas makeup through a mercury diffusion cell. The diffusion cell contains either an elemental mercury permeation tube or mercuric chloride (HgCl<sub>2</sub>) crystals maintained at an elevated temperature. For these runs the simulation gas will be spiked only with oxidized mercury from HgCl<sub>2</sub> crystals. In actual practice, the oxidized mercury source produces a small amount of elemental mercury in the simulation gas; about 5% the total mercury in the flue gas entering the scrubber is in the elemental form. Four parallel mercury diffusion cells, each containing mercuric chloride crystals, provide the mercury content of the simulation gas.



**Figure 2. Bench-scale FGD Apparatus**



**Figure 3. Bench-scale Simulation Gas Mixing Apparatus**

The wet scrubber uses a “bubbler” type gas contactor. Low slurry levels in the bubbler simulate conventional spray or tray contactors (e.g., 4 in. H<sub>2</sub>O [1 kPa] gas pressure drop) and high slurry levels can be used to simulate a high-energy venturi scrubber (e.g., 15 in. H<sub>2</sub>O [3.7 kPa] gas pressure drop). However, the normal motive force for the flow through the scrubber is the pressure of the simulation gases, so the scrubber outlet pressure is slightly positive. A venturi eductor is available to be added to the scrubber outlet gas path, so that, if desired, the scrubber outlet can be operated at negative gauge pressures.

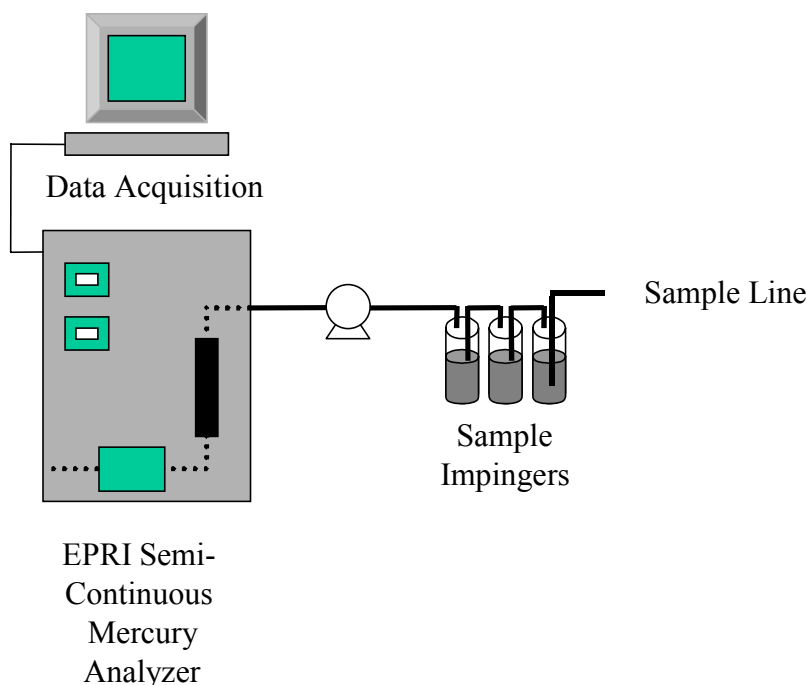
A stirred reaction tank is situated directly below and integrally mounted to the gas contactor. Slurry from the reaction tank is pumped into the contactor to maintain slurry level in the bubbler and to establish the desired liquid-to-gas ratio (L/G); spent slurry returns to the reaction tank by gravity flow. Lime or limestone reagent slurry is added to the reaction tank as needed to control pH at the set point value. A pH controller cycles the reagent makeup pump as needed. The bench-scale apparatus is heat traced, insulated and is controlled to typical full-scale wet scrubber temperatures.

The bench-scale scrubber can be operated in a continuous mode, with fresh water makeup to maintain a set weight percent solids level in the reaction tank and slurry blow down to maintain slurry level in the reaction tank. However, for this project, the runs will typically be 10 to 14 hours in duration each, and the slurry weight percent solids level and the reaction tank slurry level will be allowed to increase during the run. The slurry weight percent solids levels will typically range from 4% to 10% during these runs. Slurry will be removed for sample collection

or when necessary to lower the reaction tank slurry level, and wt% solids will be monitored visually and by gravimetric measurements.

The simulated flue gas delivery system to the bench scale wet FGD system is designed to avoid mercury loss and contamination. A heat-traced simulation gas delivery line allows the use of replaceable teflon tubing (to deal with any potential mercury contamination), and all fittings and valves in the system are either teflon or quartz components.

Mercury measurements will be made using a mercury semi-continuous emissions monitor (SCEM) developed for EPRI, as illustrated in Figure 4. In the analyzer, flue gas is pulled from the bench-scale scrubber inlet or outlet gas at about 1 L/min through a series of impinger solutions using a Teflon-lined pump.



**Figure 4. Schematic of Mercury SCEM**

To measure total mercury in the flue gas, these impinger solutions consist of stannous chloride ( $\text{SnCl}_2$ ) followed by a sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) buffer and sodium hydroxide ( $\text{NaOH}$ ). The  $\text{SnCl}_2$  solution reduces all flue gas mercury species to elemental mercury. After passing through the  $\text{SnCl}_2$  impinger, the gas flows through the  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$  solutions to remove acid gases, thus protecting the downstream, analytical gold surface. Gas exiting the impinger solutions flows through a gold amalgamation column where the mercury in the gas is adsorbed at less than  $100^\circ\text{C}$ . After adsorbing mercury onto the gold for a fixed period of time (typically 1 to 5 minutes), the mercury concentrated on the gold is thermally desorbed ( $>700^\circ\text{C}$ ) from the column into nitrogen. The desorbed mercury is sent as a concentrated stream to a cold-vapor atomic absorption spectrophotometer (CVAAS) for analysis. The total flue gas mercury concentration is measured semi-continuously, typically with a one- to five-minute sample time followed by a one- to two-minute analytical period.

To measure elemental mercury in the flue gas, the stannous chloride impinger is replaced with an impinger containing either tris(hydroxymethyl)aminomethane (Tris) or potassium chloride (KCl) solution. The Tris solution has been shown in other EPRI studies to capture oxidized mercury while allowing elemental mercury to pass through without being altered. KCl is used to collect oxidized mercury in the Ontario Hydro train. Mercury passing through the Tris or KCl solution to the gold is analyzed as described above and assumed to be elemental mercury only. The difference between the total mercury concentration (stannous chloride solution) and elemental mercury concentration (Tris or KCl solution) is assumed to be the oxidized mercury concentration.

Two analyzers will be used to semi-continuously monitor scrubber inlet and outlet gas mercury concentrations. The analyzers will be switched intermittently between sampling for elemental versus total mercury concentrations.

SO<sub>2</sub> detection tubes will also be used periodically during the testing, to quantify SO<sub>2</sub> removal across the bench-scale absorber. Overall SO<sub>2</sub> removal levels are typically 90% or greater. Aliquots of the scrubber liquor will be removed from the reaction tank periodically, and analyzed by iodometric titration to determine sulfite ion concentrations. For each test condition a set of slurry and preserved FGD liquor samples will be collected and analyzed to document the end-of-test scrubber chemistry conditions.

For some tests, the UV/visible spectrophotometer described earlier in this section will be used in conjunction with the bench-scale wet FGD system to monitor the FGD reaction tank liquor for concentrations of mercury-sulfite complexes. For these tests a slipstream of slurry from the reaction tank or from the absorber effluent slurry will be filtered in line and pumped through the sample cuvette for the UV/visible spectrophotometer, then returned to the reaction tank.



## RESULTS AND DISCUSSION

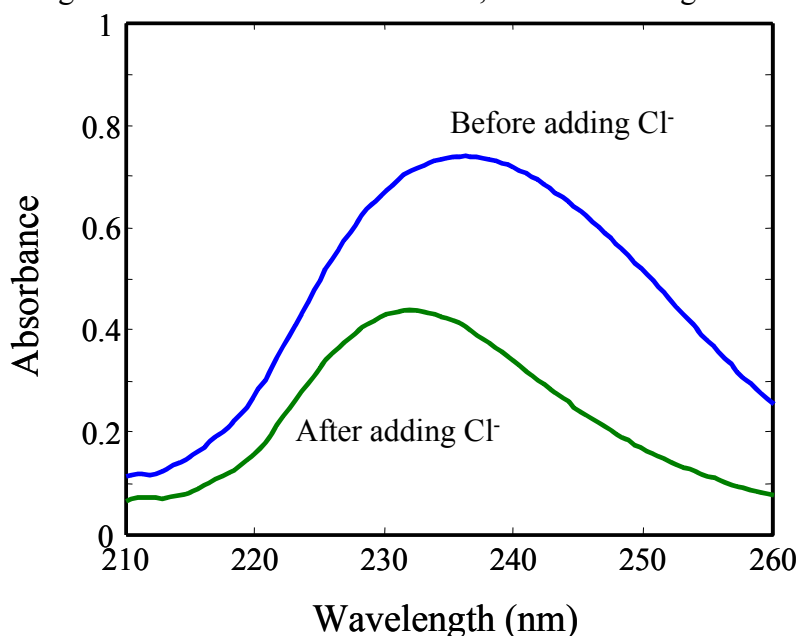
This section provides details of technical results for the current reporting period, April 1, 2005 through September 30, 2005. The technical results presented are from the Task 2 reaction kinetics investigations.

### Task 2: Kinetic Data Gathering and Model Development

#### *Kinetics Results for Solutions with Chloride and Other Complexing Agents*

In the last semi-annual report we showed how relatively low concentrations of chloride had a significant effect on the rate of mercuric ion reduction by sulfite.<sup>1</sup> Figure 9 of that report showed a smaller initial absorbance jump (believed to be due to the formation of mercuric disulfite [ $\text{Hg}(\text{SO}_3)_2^{-2}$ ]) when sulfite was added to a solution containing chloride ion, compared to results for solutions with no chloride present. Figure 9 also showed a major slowing of the rate of decomposition of the mercuric disulfite complex ( $k_{\text{obs}}$  decreasing by a factor of 25 with chloride present) as indicated by the rate of decay of that absorbance.

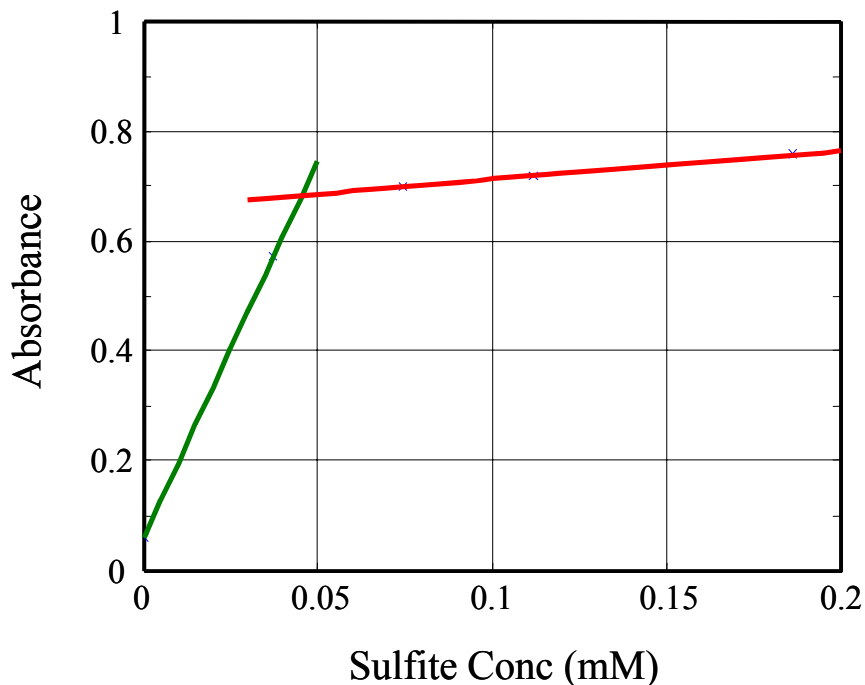
Figure 10 of that report showed results from a run that has substantial diagnostic importance. The run was started with mercuric ion and sulfite ion, but no chloride present; chloride was injected about 70 seconds after the start. When the chloride was injected there was an immediate sharp drop in absorbance, and then a change to the much slower decay of absorbance as seen in runs where chloride was present from the beginning. Further examination of the complete spectra from this previous run showed that there was a small but definite shift of about 4-5 nm in the spectral peak wavelength when the chloride was added, as shown in Figure 1 below.



**Figure 1. Shift in UV Spectra on Adding 10 mM Chloride to pH 3.0, 1.0 mM Sulfite, 40 microM  $\text{Hg}^{+2}$  Solution at 55 °C**

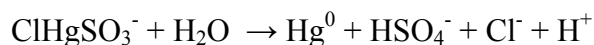
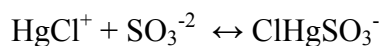
This shift was essentially completed during the 5 seconds that elapsed between spectrum acquisition. This same difference in spectral peak wavelength is noted in the individual runs done with and without chloride addition. The peak values occur at approximately 232 nm with chloride and 237 nm without chloride. This behavior suggested the formation of a different complex than the  $\text{Hg}(\text{SO}_3)_2^{-2}$  complex formed in the absence of chloride.

Inspection of analytical chemistry literature showed that mixed chloride-sulfite mercuric complexes have been suspected in analytical methods for  $\text{SO}_2$  that use tetrachloromercurate as an absorbent. Dasgupta and DeCesare assigned a spectral peak similar to the one we observed to the complex  $\text{ClHgSO}_3^-$ , but did not investigate it in detail.<sup>2</sup> We have been able to "titrate" sulfite into a solution of mercuric ion with a low concentration of chloride present. This was done at a low temperature of 10 °C to minimize mercury reduction. As shown in Figure 2, the absorbance increases rapidly as sulfite is added up to about 0.04 mM sulfite, which is equal to the original concentration of mercuric ion, then changes much more slowly with further increases in sulfite concentration.



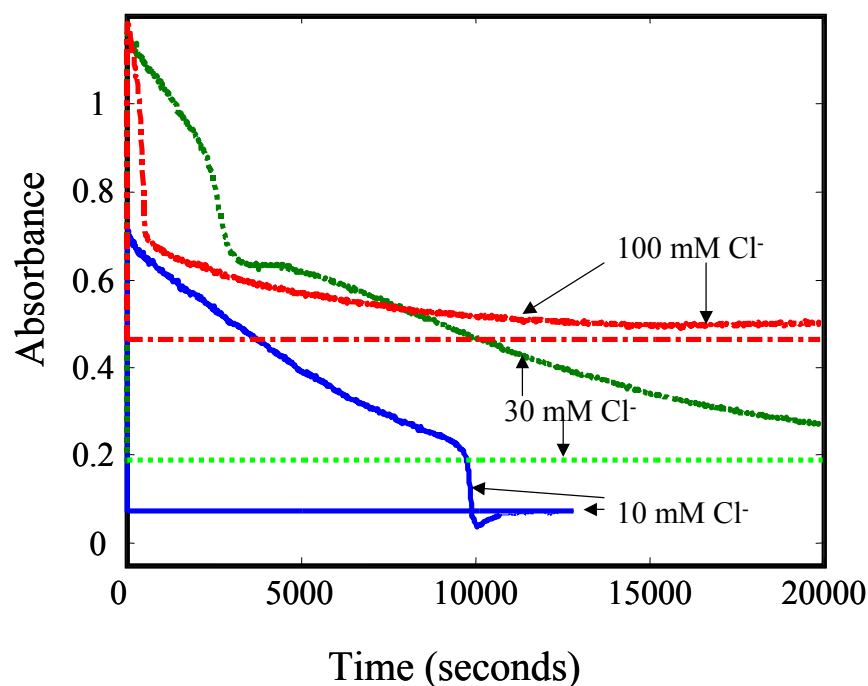
**Figure 2. Absorbance at 232 nm During Addition of Sulfite to a Solution Containing 1.0 mM NaCl, 40 microM  $\text{Hg}^{+2}$  at pH 3.5 and 10 °C**

This is consistent with the formation of a 1:1 complex between a chlorinated  $\text{Hg}^{+2}$  species and  $\text{SO}_3^{-2}$ , rather than the 2:1 complex between  $\text{Hg}^{+2}$  and  $\text{SO}_3^{-2}$  to form mercuric disulfite. We have obtained good modeling simulations of the basic rate phenomena in low chloride solutions by adding the following reactions to the model.

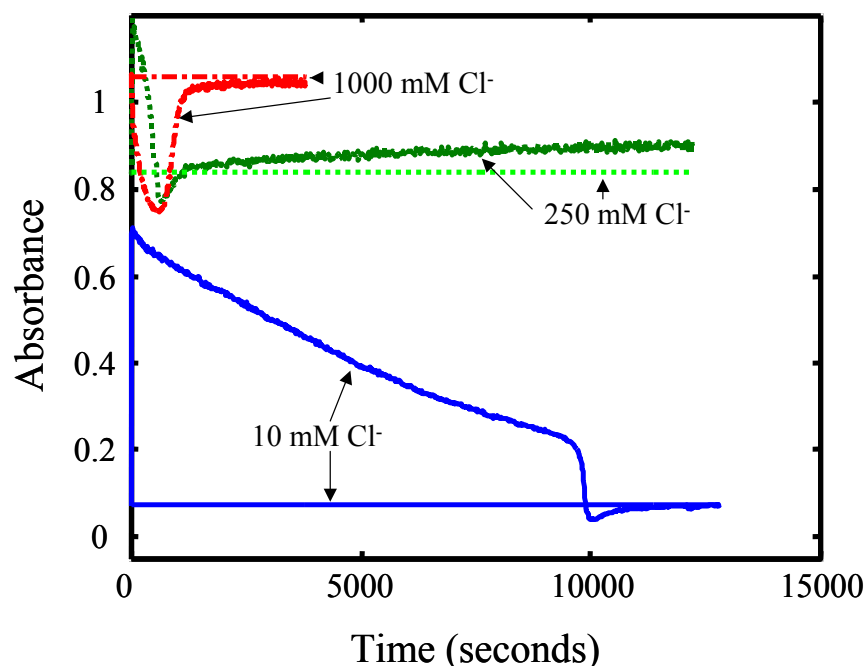


The chloride ion attached to the mercury apparently slows the decomposition of the complex by a very substantial amount. The “monosulfite” complex,  $\text{HgSO}_3$ , is thought to decompose much faster than the disulfite complex,  $\text{Hg}(\text{SO}_3)_2^{-2}$ , which, we now propose, in turn decomposes or disassociates to  $\text{HgSO}_3$  much more rapidly than the complex containing chloride.

At higher chloride concentrations the results become increasingly complicated. Typical spectrophotometric results obtained at 10, 30, and 100 mM chloride concentrations taken at wavelengths of 231, 232, and 232 nm, respectively, are shown in Figure 3. Results obtained at 250 and 1000 mM chloride taken at 230 and 231 nm are shown in Figure 4 along with the 10 mM results from Figure 3 for comparison. All of these runs were initiated by injection of sulfite to a cuvette containing chloride and mercuric ions at "t = 0." Spectra were taken at 5 second or 10 second intervals. The absorbances in these two figures were taken from the average peak wavelength values during the run. The peak wavelengths varied somewhat during the runs but were generally from 230-235 nm.



**Figure 3. Rate Curves for Addition of 1.0 mM Sulfite to Solutions Containing 10 mM, 30 mM, and 100 mM Chloride (55 °C, pH 3-3.5, 40 microM  $\text{Hg}^{+2}$ )**



**Figure 4. Rate Curves for Addition of 1.0 mM Sulfite to Solutions Containing 10 mM, 250 mM, and 1000 mM Chloride (55 °C, pH 3-3.5, 40 microM  $\text{Hg}^{+2}$ )**

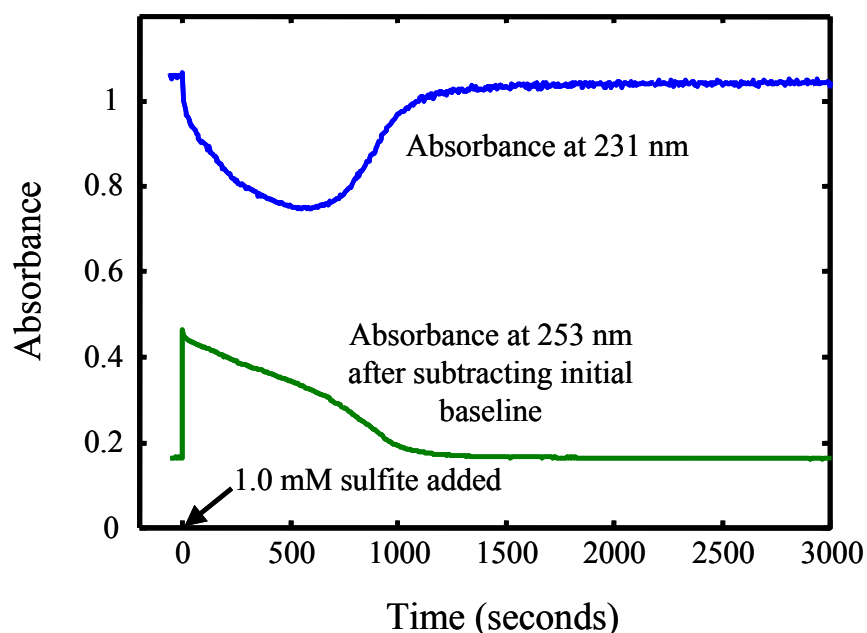
The runs represented in these two figures were done at 55 °C with 40 microM  $\text{Hg}^{+2}$  and 1.0 mM sulfite added at time zero. No pH buffer was used and the pH for individual runs varied from 3-3.5, but the variation from start to end of any given run was usually less than 0.2 pH units. The initial baseline absorbances with chloride added are shown as horizontal lines in both figures. At the lowest chloride concentration, the baseline absorbance by mercuric chloride complexes is fairly small, but it becomes quite large at higher chloride concentration. This effect is nonlinear because the monochloro- and dichloromercuric complexes have fairly low molar light absorptivities, while the trichloro- and tetrachloromercuric complexes have high molar light absorptivities. In 10 mM chloride the primary mercury species is the dichloromercuric complex,  $\text{HgCl}_2$ ; in 1000 mM chloride the tetrachloromercuric complex,  $\text{HgCl}_4^{-2}$  predominates. The tetrachloromercuric complex has an absorptivity slightly higher than the disulfitomeric complex ( $\text{Hg}(\text{SO}_3)_2^{-2}$ ) and it peaks at nearly the same wavelength, 231 nm.

In Figure 3, the 10 mM results are explainable by the formation and decay of the  $\text{ClHgSO}_3^-$  complex as described above, up to the point of the fast drop in absorbance seen at about 10,000 seconds. This drop actually goes below the initial absorbance baseline due to chloromercuric complexes but then returns to near that baseline at longer times. The fact that the absorbance returns to baseline levels might call into question whether any net reduction of  $\text{Hg}^{+2}$  occurred. However, stripping experiments carried out under similar conditions definitely show formation and release of elemental mercury, as will be described below.

The 30 mM chloride run shows an initial increase in absorbance that is larger than can be explained by formation of  $\text{ClHgSO}_3^-$ . This is followed by a steady decay then a "drop," a short plateau, and a slow steady decay that had not reached the initial baseline after 20,000 seconds.

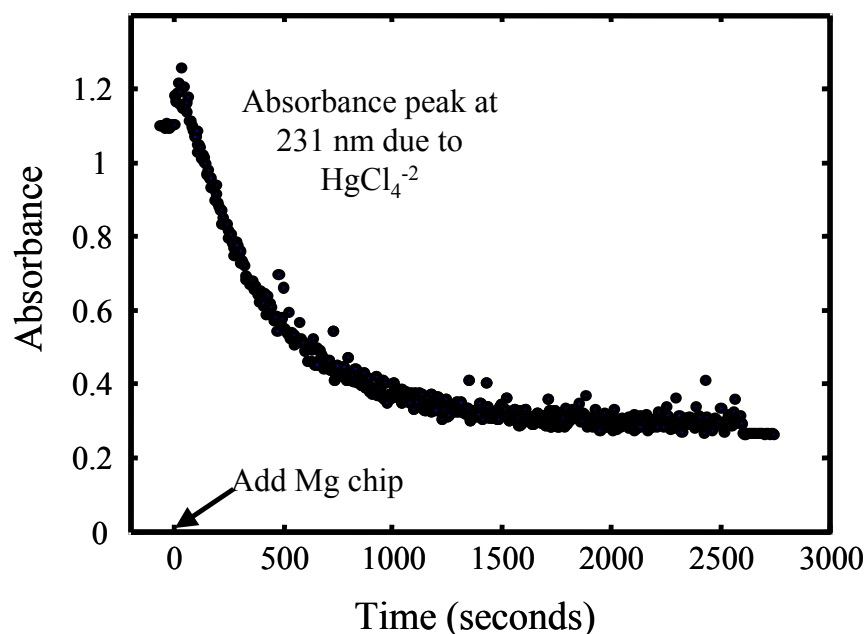
The 100 mM chloride case shows a smaller initial increase on sulfite addition than does the 30 mM case, but a much more rapid initial drop followed by a very slow decay which was still approaching the initial baseline after 20,000 seconds. The 250 mM case shows a yet smaller initial increase when sulfite is added but a rapid drop similar to the 100 mM case, although it goes below the initial baseline then slowly increases to somewhat above it.

The 1000 mM chloride case does not show any increase in absorbance when sulfite is added. Instead, the absorbance decreases to a minimum then increases back to near the initial baseline value. Figure 5, below, shows the 1000 mM chloride results at shorter times along with the growth and decay of a "shoulder" peak at 253 nm. The increase and decay of the absorbance at 253 nm appears to be roughly correlated with the opposite changes occurring in the 231 nm spectral region and could thus be due to a reaction intermediate.



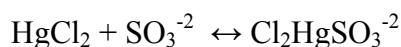
**Figure 5. Rate Curves at Two Wavelengths on Addition of 1.0 mM Sulfite to Solution Containing 1000 mM Chloride (55 °C, pH 3.5, 40 microM Hg<sup>+2</sup>)**

As mentioned above, this return to the baseline absorbance suggests the possibility that mercuric species are not being reduced to form elemental mercury. As a check on the difficulty of reducing mercuric species at high chloride concentration, we looked at the reduction of mercuric species in 1000 mM chloride using a chip of magnesium metal as the reductant instead of sulfite. There is a small rise in absorbance due to blocking of light by the chip. But aside from this, the results in Figure 6 show a smooth and fairly rapid decrease in total absorbance due to the chloromercuric species, as would be expected from reduction of these species. Thus, there does not appear to be an inherent barrier to reduction of Hg<sup>+2</sup> at high chloride concentrations.



**Figure 6. Effect of Adding a Magnesium Chip to a Solution Containing 1.0 M NaCl and 40 microM Hg<sup>+2</sup> at 55 °C**

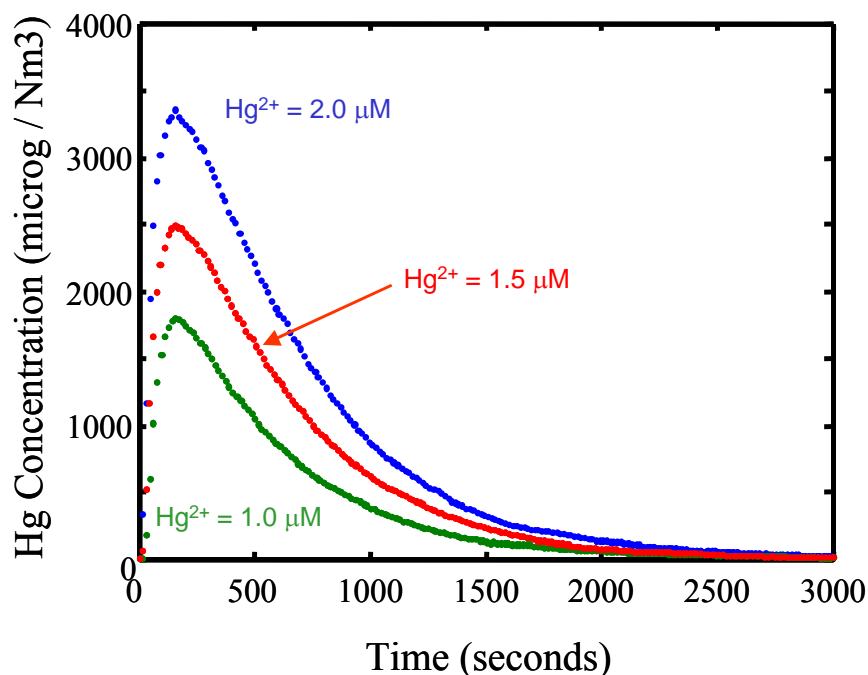
We are in the process of unraveling the possible interplay between kinetics and equilibria of formation of multiple complexes of Hg<sup>+2</sup> with Cl<sup>-</sup> and SO<sub>3</sub><sup>-2</sup>. For example, we are looking at adding to the kinetics model the formation of another mercury complex containing both chloride and sulfite, along with its decomposition reaction, as shown below:



Initial modeling and lab measurements to determine the formation constants of the complexes indicate that this may help fit the observed data to a kinetics model, although the formation of the dichloro complex is less favored than the formation of the monochloro complex. At high chloride concentrations the chloromercuric complexes alone tend to dominate over the formation of mercuric sulfite and mercuric disulfite, and "shut down" the other reactions. However, it is difficult to interpret and determine all of the necessary information based on spectrophotometric results alone. As described below, Hg<sup>0</sup> stripping rate measurements verify and extend the spectrophotometric results.

The stripping rate method measures the amount of gas phase elemental mercury produced by the reactions as a function of time. The apparatus was modified since the last report to measure gas phase mercury concentrations continuously without using absorption/stripping of the mercury on/from gold. The gas phase Hg<sup>0</sup> is measured directly in a 17.5 cm flow tube using a 254 nm mercury lamp source and photomultiplier detector. The absorptivity of gas phase Hg<sup>0</sup> was taken as 4.1 x 10<sup>6</sup> L/(gmole cm).<sup>3</sup> This approach provides a more direct measurement and much shorter time between measurements. It also makes the equipment simpler and more reliable.

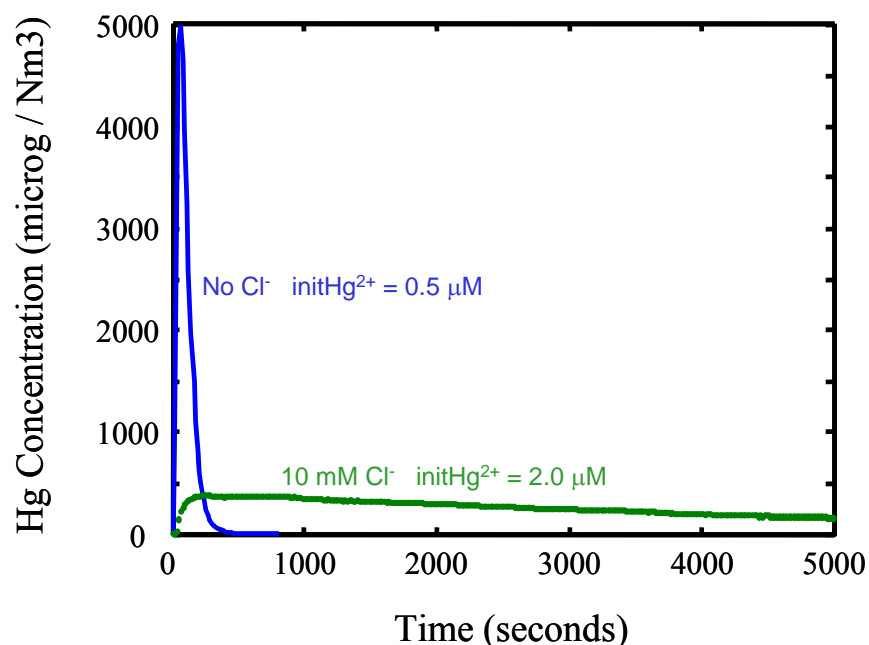
Typical results obtained with this equipment are shown in Figure 7 for three different levels of  $\text{Hg}^{+2}$  injected at  $t = 0$ . These runs were done at 55 °C with 124 ppm  $\text{SO}_2$ , balance  $\text{N}_2$  in the gas passing through the absorber, sulfite level of 1.3 mM, and pH of 3.1.



**Figure 7.  $\text{Hg}^0$  Stripping Kinetics Results for Addition of 1.0, 1.5, and 2.0 mM  $\text{Hg}^{+2}$  to Solution Containing 1.3 mM Sulfite at pH 3.1, with 124 ppm  $\text{SO}_2$  in Gas Phase at 55 °C**

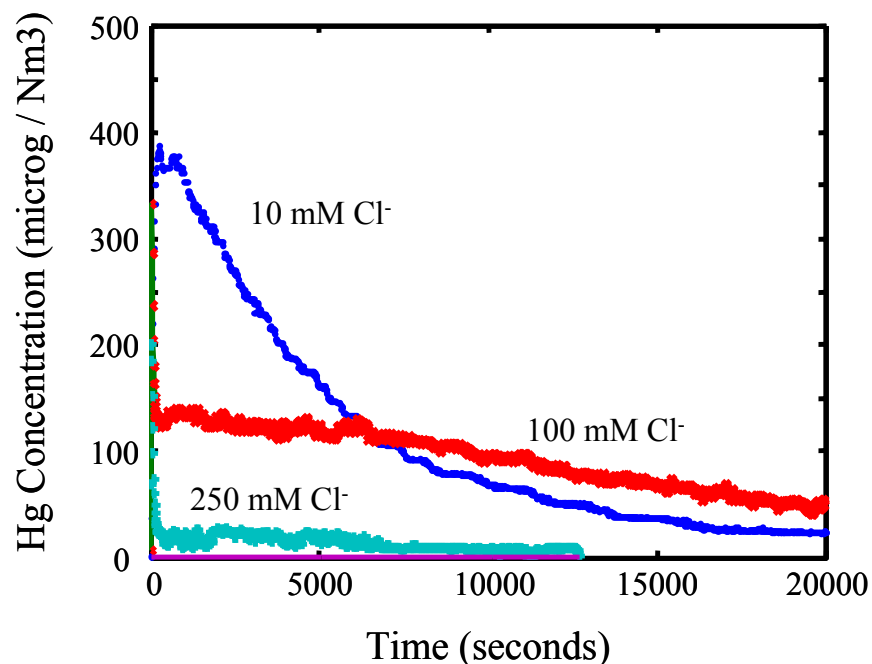
As shown in Figure 7, elemental mercury starts to evolve at once, reaches a peak, and then shows a decline similar in shape to the spectrophotometric decay curves of the mercuric sulfite complex that have been shown previously. Values of the "observed" rate constant,  $k_{\text{obs}}$ , were calculated from the slope of the natural log of absorbance versus time in the absorbance decay region of the figure. For these three runs the  $k_{\text{obs}}$  was essentially the same,  $2.0 \pm 0.15 \times 10^{-3} \text{ sec}^{-1}$ , as would be expected for a reaction that is first order in dissolved  $\text{Hg}^{+2}$  overall. This is also in very good agreement with the  $k_{\text{obs}}$  calculated from the corresponding spectrophotometric experiment,  $3 \times 10^{-3} \text{ sec}^{-1}$  (which would be expected to be somewhat higher since it was done at lower sulfite concentration, 1.0 mM vs. 1.3 mM).

The effect of adding 10 mM chloride on the stripping kinetics is shown in Figure 8. As expected from the spectrophotometric work, both the amount of Hg stripped and the rate of stripping is lowered drastically. The average  $k_{\text{obs}}$  from three stripping runs is  $1.7 \pm 0.7 \times 10^{-4} \text{ sec}^{-1}$  and is again in good agreement with the spectrophotometric value of about  $2 \times 10^{-4} \text{ sec}^{-1}$ .



**Figure 8. Stripping Kinetics Results with and without 10 mM Chloride at 55 °C**

A comparison of stripping kinetics for runs with 10 mM, 100 mM, and 250 mM chloride is shown in Figure 9. The 10 mM chloride run started with an injection of 2.0 microM  $\text{Hg}^{+2}$ ; the 100 and 250 mM chloride runs used ten times the initial amount of mercury, from a 20 microM  $\text{Hg}^{+2}$  injection, to produce measurable vapor phase  $\text{Hg}^0$  concentrations because of the effects described below.

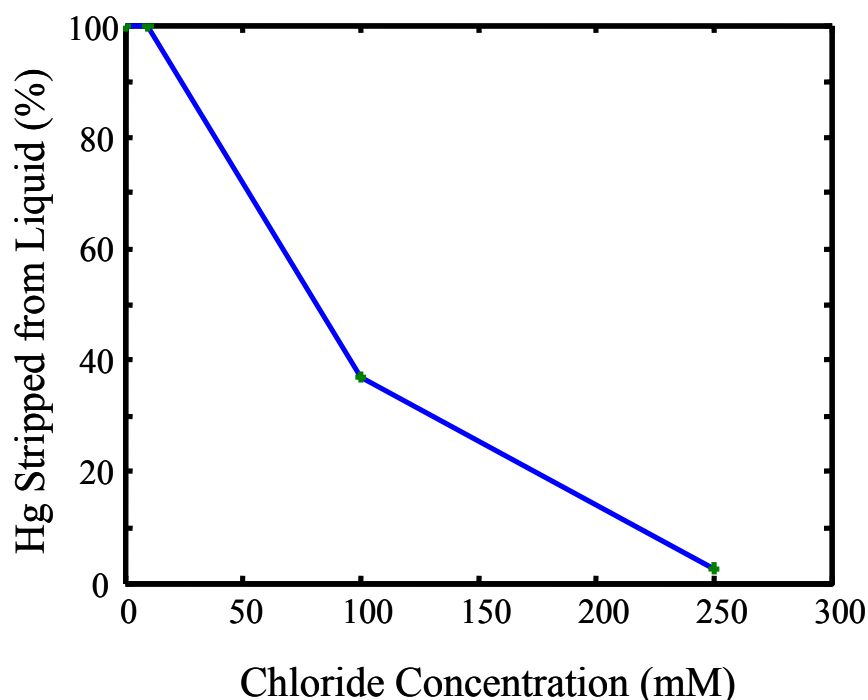


**Figure 9. Stripping Kinetics Results with 10 mM, 100 mM and 250 mM Chloride at 55 °C**



Again, the data in this figure show that each increasing level of chloride drastically decreases the overall amount and rate of evolution of  $\text{Hg}^0$  from the solution. Also note that there is typically a "spike" of  $\text{Hg}^0$  released at the very start of the run. It is tempting to associate this with the spike in absorbance seen at the start of many of the high chloride spectrophotometric runs, but more work is needed to establish a relationship.

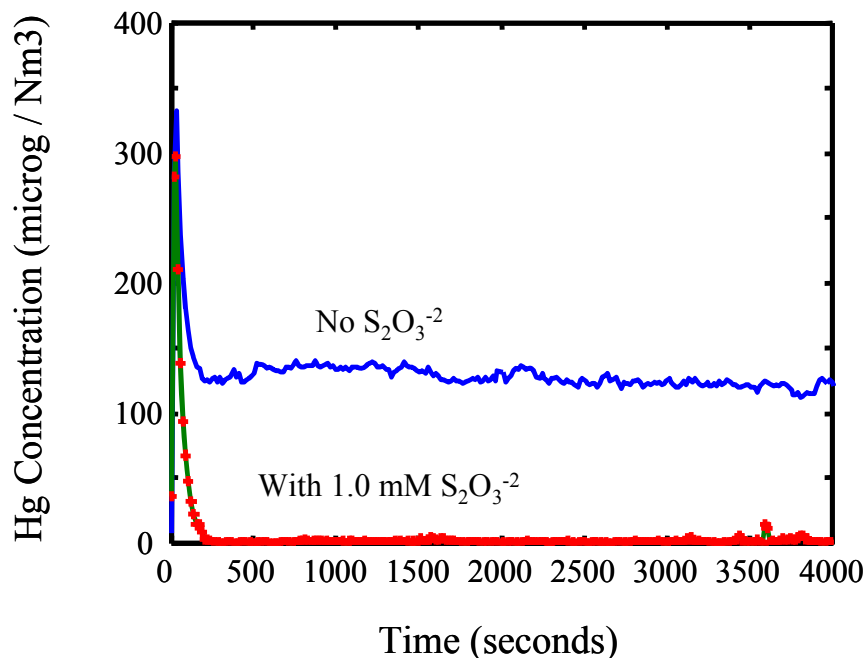
The sorbent liquids from the stripping kinetics runs were analyzed for mercury after each run by cold vapor atomic absorption. As shown in Figure 10, over 99.5% of the mercury was stripped out of the solution in the 0 and 10 mM chloride cases. For the 100 mM chloride case only 37 % of the added mercury was stripped and for the 250 mM chloride case less than 3 % was stripped after a total run duration of more than 50 hours. To put these chloride concentrations into the perspective of typical FGD liquor chloride concentrations, 10 mM (~350 ppm) would represent a very low FGD chloride ion concentration, while 100 mM (~3500 ppm) would represent a mid-range value for an FGD system with a moderate chloride purge rate. The highest value of 250 mM (~8800 ppm) is not atypically high for FGD systems with a lower chloride purge rate (e.g., systems that produce wallboard-grade gypsum) which can range up to 10 times that chloride concentration.



**Figure 10. Percentage of Mercury Stripped from Solution, as a Function of Chloride Concentration**

We have briefly looked at the effects of thiosulfate ion (present in inhibited oxidation FGD liquors) on mercury reduction using the stripping kinetics method. The mercuric-thiosulfate complexes are strong and have high UV absorbance, complicating spectrophotometric measurement even at low thiosulfate concentrations. Results of a stripping kinetics using 1.0 mM thiosulfate added to a 100 mM chloride solution are compared in Figure 11 to those obtained without thiosulfate but also with 100 mM chloride; both were spiked with 20 microM

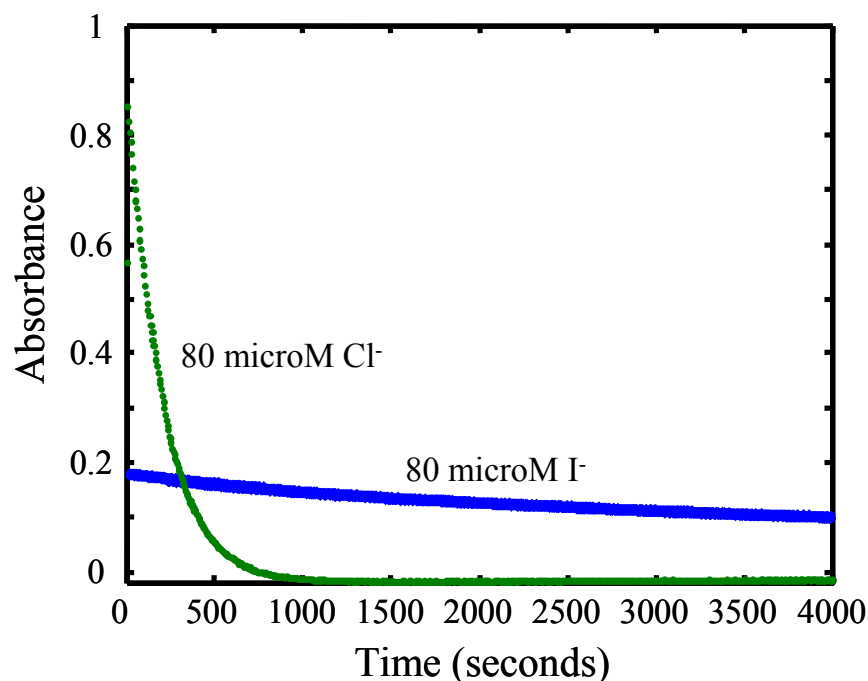
$\text{Hg}^{+2}$ . Note that 1.0 mM of thiosulfate (~110 ppm) is a relatively low concentration compared to typical values in inhibited oxidation FGD liquors, where values of 10 to 30 mM are common.



**Figure 11. Effect of Adding 1.0 mM Thiosulfate to a 100 mM Chloride Solution on  $\text{Hg}^0$  Stripping Kinetics**

As can be seen, the initial sharp stripping peak is very similar in the two cases. In the case without thiosulfate there follows a period of fairly steady evolution of  $\text{Hg}^0$ . In the thiosulfate case, however, the  $\text{Hg}^0$  evolution essentially goes to zero after the initial spike. Analysis of the thiosulfate solution for mercury concentration indicated that less than 10% of the original mercury had been stripped after over 21 hours. Less than 0.1% of the added mercury could be accounted for in the gas phase for this run. Thus, it appears that even low concentrations of thiosulfate inhibit  $\text{Hg}^0$  evolution under these conditions, probably due to formation of mercuric-thiosulfate complexes which are stable and which block the more rapid reduction pathways involving chloromercuric sulfite complexes.

Another interesting example of effects of a strong complexing agent is shown in a run done with only 80  $\mu\text{M}$  iodide (~10 ppm), which is compared to results with 80  $\mu\text{M}$  of chloride (~ 3 ppm) under the same pH 3.0, 1.0 mM sulfite, and 55 °C conditions in Figure 12.



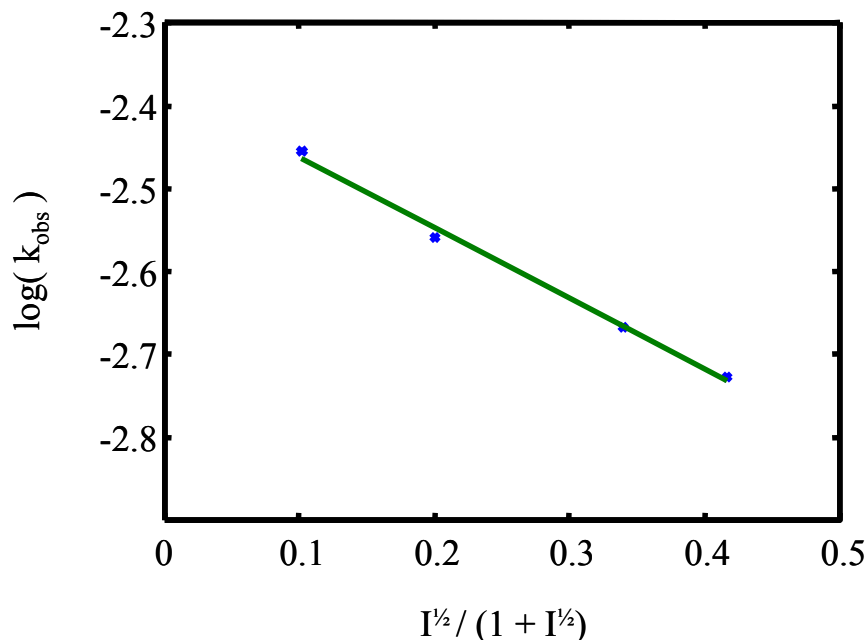
**Figure 12. Comparison of Effects of 80  $\mu\text{M}$  Iodide and 80  $\mu\text{M}$  Chloride on Kinetics of Mercuric Ion Reduction**

The response with 80  $\mu\text{M}$  chloride is similar to and about as fast as without chloride, indicating that chloride cannot compete very well with sulfite in complexing (and reducing) mercuric ion at this low concentration. However, iodide, which is known to be a very strong complexing agent for mercuric ion, reduces the rate of reaction substantially. The  $k_{\text{obs}}$  for the run with iodide is  $1.3 \times 10^{-4} \text{ sec}^{-1}$ , similar to but still somewhat slower than that obtained for the 10 mM chloride runs.

### *Reaction Mechanism Experiments*

A number of experiments were performed to gather information on possible re-emission reaction pathways and mechanisms. This included measuring ionic strength effects, looking for various intermediates, adding  $\text{O}_2$  to the system, and investigating possible measurement artifacts involving photochemical effects and buffer stability.

Ionic strength is related to the total concentration of dissolved ionic species in the liquid. Determining ionic strength effects is often helpful for determining reaction mechanisms for model development. The rate of reaction in a solution can be increased, decreased, or unchanged with increasing ionic strength, depending on whether the reactants in a rate-determining reaction step have the same charge, an opposite charge, or if one reactant is uncharged. We have looked at the effects of ionic strength by measuring rate constants for the disappearance of mercuric disulfite from solution as a function of added electrolyte concentration, using an "inert," non-complexing electrolyte, sodium perchlorate ( $\text{NaClO}_4$ ). Results obtained at pH 3.0, 55  $^\circ\text{C}$ , 1.0 mM sulfite, 40  $\mu\text{M}$   $\text{Hg}^{+2}$  in the absence of chloride are shown in Figure 13.

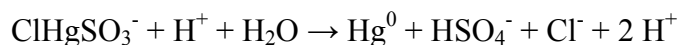


**Figure 13. Ionic Strength Dependence of  $k_{\text{obs}}$  (55 °C, 1.0 mM sulfite, pH 3.0, 40 microM  $\text{Hg}^{+2}$ )**

This shows that the rate decreases with increasing salt concentration. The plotted form uses the Debye-Huckel-Bronsted relation for the "primary salt effect," where  $k$  is the observed rate constant,  $k_0$  is the rate constant at zero ion strength,  $I$  is the ionic strength defined in terms of the charges on the ions ( $z_i$ ) and molar concentrations of the ions ( $M_i$ ), and  $A_\gamma$  is a temperature-dependent constant = 0.5371 at 55 °C.

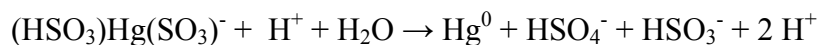
$$\log k = \log k_0 + 2 A_\gamma z_A z_B I^{1/2} / (1 + I^{1/2}) \quad \text{where: } I = \frac{1}{2} \sum z_i^2 M_i$$

A value of  $z_A z_B = -0.79$  was obtained from the slope of the curve. A value of -1 indicates that two species, one with a +1 charge and the other with a -1 charge, are involved in a rate-determining step, and that is probably the case for the experimental result. The value obtained in the presence of 10 mM chloride is slightly lower, -0.69. The most likely reactant having a charge of +1 is hydrogen ion. For the case with chloride, a candidate for the -1 charged ion is  $\text{ClHgSO}_3^-$ , and a possible rate-determining reaction is:



Since hydrogen ion is not consumed in the overall reaction, this would constitute hydrogen ion catalysis.

However, the data shown in Figure 13 are without chloride in the solution. It is more difficult to identify a candidate -1 charged species for the case without chloride, since the two reactive complexes are usually assumed to be  $\text{HgSO}_3$  and  $\text{Hg}(\text{SO}_3)_2^{-2}$ . However it is quite possible that the disulfite complex is protonated, giving the singly charged species  $(\text{HSO}_3)\text{Hg}(\text{SO}_3)^-$  which reacts with  $\text{H}^+$  and water similarly to the chloromercuric sulfite.

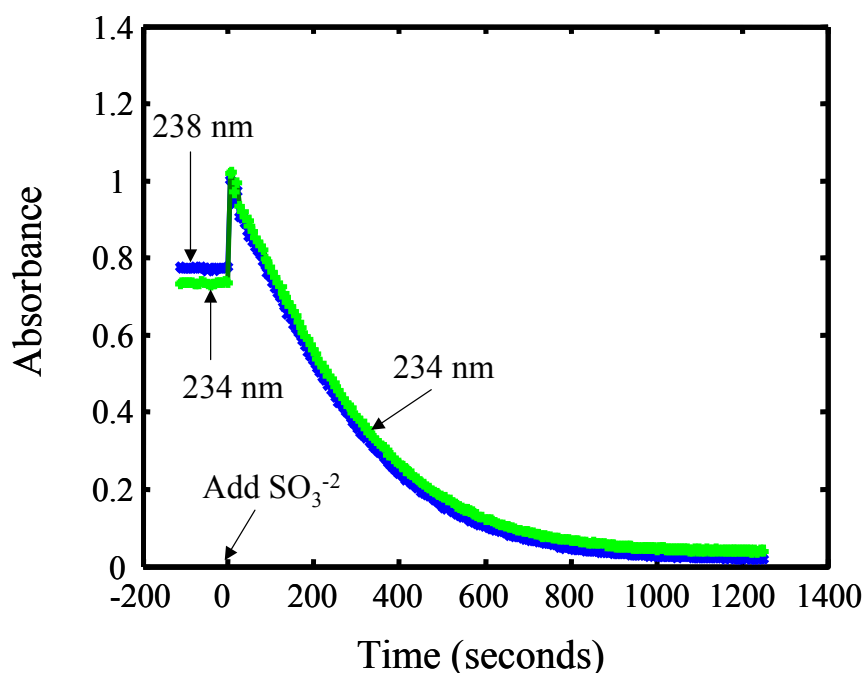


This reaction could have another interesting pathway involving simultaneous electron transfer, one from each of the two sulfite ligands, to the mercuric center. Although speculative, this might explain why replacing a sulfite with a chloride on the mercury center slows down the reduction.

As noted in the last report, under "ideal" conditions at low pH (3), low sulfite, and no other complexing agents, the reduction of  $\text{Hg}^{+2}$  by sulfite produces textbook first order decay curves. However at other conditions, particularly those which slow down the reaction, the shape of the absorbance - time curve starts to deviate significantly from what one would expect from a simple first order reaction, and significant changes are often seen in the time behavior during the run. This is usually a sign that reaction intermediates are being formed that either inhibit or accelerate the overall reaction.

The overall reaction of  $\text{Hg}^{+2}$  with sulfite involves a two-electron change for both  $\text{Hg}^{+2}$ , going to  $\text{Hg}^0$ , and for sulfite, going to sulfate ( $\text{S}^{+4}$  to  $\text{S}^{+6}$ ). Potential intermediates thus include those formed by one-electron steps such as mercurous ( $\text{Hg}^{+1}$ ) species and oxysulfur radicals such as the sulfite radical anion,  $\cdot\text{SO}_3^-$ .

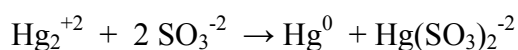
A spectrophotometric experiment was done starting with 40  $\mu\text{M}$  mercurous ion ( $\text{Hg}_2^{+2}$ ) instead of the usual 40  $\mu\text{M}$   $\text{Hg}^{+2}$ , at 55 °C and pH 3.0, with addition of 1.0 mM sulfite to start the run as usual. The initial mercurous perchlorate solution was prepared by stirring a de-aerated 0.01 M  $\text{Hg}(\text{ClO}_4)_2$  solution over a mercury pool for 48 hours and dilution. The results are shown in Figure 14.



**Figure 14. Rate Curve at Two Wavelengths for the Addition of Sulfite to a Solution Initially Containing Mercurous Ion at 55 °C and pH 3.0**

Mercurous ion has a significant absorption peak at 238 nm and this is indicated by the absorbance before addition of sulfite. Examination of the individual spectra shows a distinct change in spectra from one having a peak of 238 nm (i.e., the absorbance is greater at 238 nm than at 234 nm) at an absorbance of 0.77 to one having a peak at 234 nm (greater absorbance than at 238 nm) and absorbance of 1.00, occurring within the 5-second period between spectrum acquisition. The latter spectrum corresponds with 36  $\mu\text{M}$  of the mercuric disulfite complex. The present form of the URS kinetics model predicts a nearly identical starting concentration of 35  $\mu\text{M}$  when starting with  $\text{Hg}^{+2}$  rather than mercurous ion in solution. The ensuing decay rate is also essentially the same as would be expected for mercuric disulfite under these conditions.

These results can be explained by rapid and practically complete disproportionation of mercurous ion induced by sulfite, as shown in the following reaction.



This would indicate that while the mercurous ion  $\text{Hg}_2^{+2}$  may still be a transient intermediate, it probably does not build up to significant concentration levels. There was a persistent residual absorbance peak at 223 nm with absorbance of 0.20 after the main reactions were completed in this run that is not seen in runs started with  $\text{Hg}^{+2}$ . Its origin is not known but might be associated with the  $\text{Hg}^0$  product, perhaps in colloidal form.

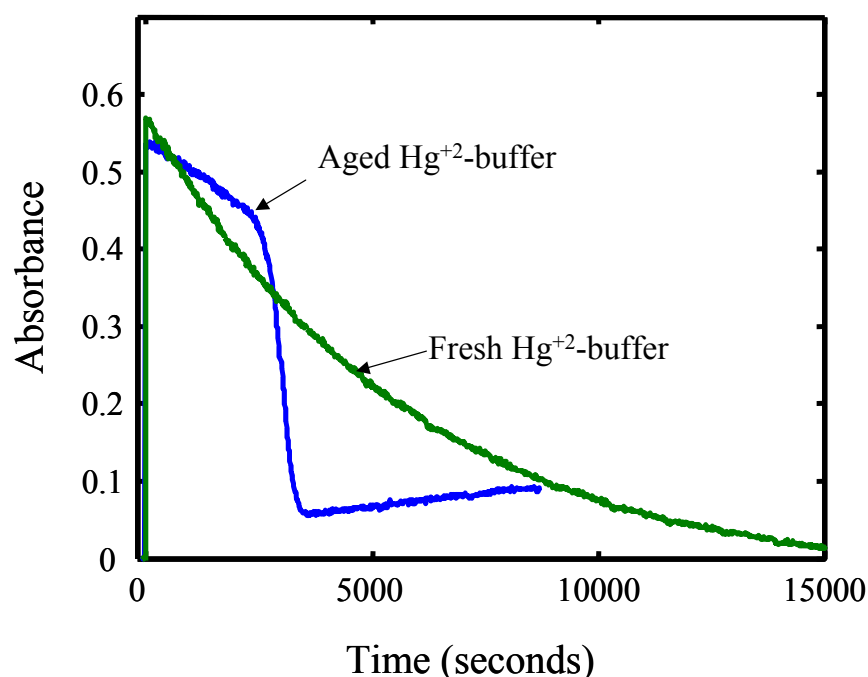
Sulfite radical anion is thought to be an important intermediate in FGD sulfite oxidation chemistry. Although the direct reaction of oxygen with sulfite is quite slow, it is catalyzed by transition metal ions (such as iron, manganese, and copper) whose oxidized forms can oxidize sulfite to the radical ion. Since sulfite is undergoing oxidation in the reactions we are studying, the sulfite radical ion  $\cdot\text{SO}_3^-$  could be formed. This species has an absorption peak at 255 nm, but its absorptivity is low (approximately 1000 L/(gmole cm)) so it would be difficult to detect in the presence of other UV absorbing species such as we have in these experimental procedures. Since involvement of  $\cdot\text{SO}_3^-$  should be indicated by sensitivity of the results to oxygen, we instituted stringent pre-purging of reaction cuvette and restriction of air access to reagents before the run, but did not see any noticeable effect. We then did a run using intentionally aerated solutions and obtained virtually the same spectrophotometric results and  $k_{\text{obs}}$  as usual. Finally, we did  $\text{Hg}^0$  stripping kinetics runs with pure oxygen instead of nitrogen as the major gas. While the  $k_{\text{obs}}$  values were somewhat lower (by an average of 32%) with oxygen than without, no unusual changes in shape of the rate curves were apparent. As with mercurous ion, while this does not rule out the transient formation of  $\cdot\text{SO}_3^-$ , it does not appear as if this species plays a major role as judged by aeration effects. Also, we need to redo some of these checks with chloride present.

### *Checks for Experimental Artifacts*

Mercury compounds are known to undergo photochemical reactions. Although the light source used to make our spectrophotometric measurements is low intensity, we checked to see if it could be causing photochemical reactions that might lead to complex kinetic behavior. To check this we repeated a run with the UV light intensity decreased by a factor of 10 using simple plastic

filters. Although there were some minor differences, the "induction time" and sharp drop in absorbance were similar for the two runs, indicating that photochemical effects are probably minor.

We found one effect that is definitely an experimental artifact, which is also instructive. Many of the initial runs used a pH 3.0 buffer made from 10 mM chloroacetate/chloroacetic acid. This is a standard buffer and is reasonably stable as a stock solution. However, we found that buffer solutions to which mercuric ion had been added and allowed to stand for several days gave strange but reproducible results, as shown in Figure 15. In the figure, both solutions had 10 mM NaCl, 1.0 mM sulfite, 10 mM pH 3.0 buffer, and 50 mM NaClO<sub>4</sub>, and were run at 55 °C.



**Figure 15. Comparison of Time Profiles for Fresh Chloroacetate Buffer and Buffer Exposed to Mercuric Ion for Several Days**

No such problems have been experienced with acetic acid buffers used at pH 4-5 or with unbuffered solutions. In retrospect, mercuric ion is probably a good catalyst for the hydrolysis of chloroacetic acid, since it would tend to extract the chlorine atom, leaving a carbonium ion that is very labile for hydrolysis. The likely product would be glycolic acid or glycolate. This species might then chelate or react with mercuric ion, leading to the effects shown. The "bad buffer" compound noticeably enhances the "inductive time" behavior, leading to a sharp drop in absorbance at times much shorter than normally seen in 10 mM chloride solutions.

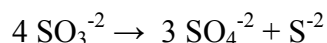
### *Kinetics Model and Future Work*

The kinetics model was described in the last semi-annual report. We have continued to update the model during this period and to examine new ideas about mechanisms, including the effect of adding different mixed chloro-sulfite mercuric complexes. We also did experimental runs that

enabled us to include better estimates of the mercuric-chloride rate constants, which are largely unreported in the literature. Work was also done on modeling the  $\text{Hg}^0$  stripping kinetics reactor as a continuous flow reactor.

The model is now able to reproduce the main part of the complexing with chloride and the various sulfite complexes. As indicated above, we as yet do not have an explanation for the "induction time" behavior. There are several other possible sources of this behavior that we can explore experimentally. One of these is buildup of elemental mercury product, which could react with mercuric complexes or reaction intermediates. Bulk phase elemental mercury is very insoluble in water ( $0.3 \mu\text{M}$  at  $25^\circ\text{C}$ ), but formation of colloidal mercury is well known in the literature. We have not observed such formation visibly, but colloids are often invisible to the eye. As a check on whether this is a viable mechanism, we will generate the colloid externally and then add some to reacting solutions to see if the rate accelerates.

We have some very preliminary spectrophotometric evidence that sulfite is being decomposed at more than stoichiometric amounts in some runs. If this is found to be the case, there is the possibility that mercury is catalyzing the disproportionation of sulfite, which is thermodynamically favored but very slow under most conditions. Complete disproportionation of sulfite is represented by:



Other reduced sulfur compounds may also be formed. These reduced sulfur species could provide a pathway for the fast reduction we see after an induction time in some runs. There is also another interesting application. Anecdotal reports of "mercuric sulfide" being formed in FGD systems is fairly common, although sulfide is not normally present in FGD liquors. However, if sulfide was formed via catalysis by mercury, it would be molecularly near the mercury and could then react with a mercury species to form  $\text{HgS}$  before being oxidized.  $\text{HgS}$  is highly insoluble and thus could be separated from the liquid phase reactions as a solid.

In addition, several other brief investigations have been suggested by the results. It will be of interest to determine the effect of adding magnesium ion, since magnesium ion is found in most FGD liquors, and there are a number of magnesium-enhanced FGD systems.  $\text{Mg}^{+2}$  forms a relatively strong ion pair with sulfite and thus may influence the mercuric reactions with sulfite. Chelating agent inhibitors such as EDTA and TMT are of apparent interest and will also be investigated. TMT has a UV absorbance that may be separated enough from those of the Hg compounds to give additional information on the mechanism of its action.



## CONCLUSION

There is ample evidence that mercury re-emission reactions are limited by kinetics rather than equilibrium. Fundamental laboratory studies of the kinetics of mercury reactions in the aqueous phase are currently being conducted as part of this project. A review of the literature produced an initial series of chemical reactions between  $\text{Hg}^{+2}$  and sulfite ion that could lead to re-emissions, and additional pathways have been identified as described here. Experimental methods have been developed using UV spectrophotometry to identify reaction intermediate species, and to track their changes in concentration as the reactions proceed. A separate but complementary method of following the rate of evolution of mercury from the liquid phase has also been developed and applied.

Using these methods, both the rate of disappearance of the mercuric disulfite complex (a major pathway for  $\text{Hg}^{+2}$  reduction) and the rate of formation of elemental mercury product can be monitored. Work is in progress to define the effects of temperature, ionic strength, initial reactant concentrations, pH, chloride, thiosulfate, and other complexing agents on the rates of these reactions, and thus on the re-emission of Hg from FGD systems.

In the last semi-annual report we showed how fairly low concentrations of chloride had a significant effect on the rate of mercuric ion reduction by sulfite. Progress has been made on explaining the effects of chloride ion on the kinetics. Evidence was found for the formation of at least one complex of mercuric ion with both sulfite and chloride. The chloride ion attached to the mercury apparently slows the decomposition of the complex by a very substantial amount, as the monosulfite complex  $\text{HgSO}_3$  is thought to decompose much faster than the disulfite  $\text{Hg}(\text{SO}_3)_2^{-2}$  complex, which in turn decomposes much more rapidly than the complex containing chloride. At higher chloride concentrations the results become more complicated as the chloride is increased from 30 to 1000 mM. Low concentrations of iodide are much more effective at slowing the reduction reactions than is chloride.

At high chloride concentrations the chloromercuric complexes alone (without attached sulfite) tend to dominate and "shut down" the mercury reduction reactions. However, it is difficult to interpret and determine all of the necessary information based on spectrophotometric results alone. Measurements of the rate of stripping of elemental mercury from solution as a function of time were used to verify and extend the spectrophotometric results. In the absence of chloride, the  $\text{Hg}^0$  stripping rate measurements confirm the first order disappearance of  $\text{Hg}^{+2}$  and equivalent rate constants are obtained for this case as well as at low chloride concentrations. At elevated chloride levels the  $\text{Hg}^0$  stripping rate measurements show a sharp initial release of elemental mercury, but then very low rates of release are observed for extended times. These results were verified by measurement of mercury retained in the liquor after the run. Low levels of thiosulfate combined with intermediate chloride levels also showed similar, very low stripping rates following an initial "spike" of elemental mercury.

Mechanistic work has continued with measurement of the ionic strength dependence of the reactions and several attempts at identifying additional reaction intermediates. This information is needed for model development since in several instances the reaction rate curves deviate significantly from simple "first order" behavior. This is to be expected for a reaction that

involves a number of individual steps instead of just one rate-controlling reaction. Investigation of the effects of inhibitors on the reaction rates and the possible disproportionation of sulfite are also planned. An existing chemical kinetics model has been adapted to the mercury-sulfite-chloride-thiosulfate system and takes into account the simultaneous occurrence of a number of reaction steps. The model will be used to design bench-scale experiments for testing as well as for prediction of kinetics in low pH regions, such as at the SO<sub>2</sub> gas-aqueous interface, which are difficult to investigate experimentally.

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